SEMICONDUCTING OXIDE NANOSTRUCTURES

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in- part of and claims priority to copending U.S.

5   utility application entitled, "Semiconducting Oxide Nanostructures," having ser. no.

10/216,696, filed on 8/8/02, which is a divisional application of U.S. Patent 6,586,095

entitled "Semiconducting Oxide Nanostructures," having serial no. 10/042,868, filed on

01/08/02, which claimed priority to copending U.S. provisional application entitled,

"Semiconductive Oxide Nanobelts," having ser. no. 60/261,367, filed January 12, 2001,

10   which is entirely incorporated herein by reference.

TECHNICAL FIELD

This disclosure is generally related to nanostructures and, more particularly, is

related to semiconductive and piezoelectric oxide nanostructures and fabrication thereof.

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BACKGROUND

Binary semiconducting oxides often have distinctive properties and can be used as

transparent conducting oxide (TCO) materials and gas sensors.   Current studies of

semiconducting oxides have been focused on two-dimensional films and zero-dimensional

20   nanoparticles. For example, fluorine-doped tin oxide films are used in architectural glass

applications because of their low emissivity for thermal infrared heat. Tin-doped indium

oxide (ITO) films can be used for flat panel displays (FPDs) due to their high electrical

conductivity and high optical transparency; and zinc oxide can be used as an alternative

material for ITO because of its lower cost and easier etchability. Tin oxide nanoparticles

can be used as sensor materials for detecting leakage of several inflammable gases owing to their high sensitivity to low gas concentrations.

In contrast, investigations of wire-like semiconducting oxide nanostructures can be difficult due to the unavailability of nanowire structures. Wire-like nanostructures have

5   attracted extensive interest over the past decade due to their great potential for addressing some basic issues about dimensionality and space confined transport phenomena as well as related applications. In geometrical structures, these nanostructures can be classified into two main groups: hollow nanotubes and solid nanowires, which have a common characteristic of cylindrical symmetric cross-sections. Besides nanotubes, many other wire-

10   like nanomaterials, such as carbides, nitrides, compound semiconductors, element semiconductors, and oxide nanowires have been successfully fabricated.

However, the nanostructures discussed above can have a variety of deficiencies. For example, often it is difficult to control the structure and morphology of many nanostructures. Further, many nanostructures are not defect and/or dislocation free.

15   These deficiencies can cause problems such as, for example, uncontrolled properties due to uncontrolled structure and/or morphology, scattering from dislocations in electric transport applications, and degraded optical properties. Thus, a heretofore unaddressed need exists in the industry to address at least the aforementioned deficiencies and/or inadequacies.

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SUMMARY

Briefly described, this disclosure provides for new types of nanostructures and

methods of fabrication thereof. A representative nanostructure includes a free-standing,

helical semiconductor oxide nanostructure. The free-standing, helical semiconductor

5 oxide nanostructure includes a nanobelt having a substantially rectangular cross-section.

The the nanobelt is about 5 nanometers to about 200 nanometers in width and about 3

nanometers to about 50 nanometers in height, and the radius of the helical semiconductor

oxide nanostructure is about 200 to 5000 nanometers.

Another representative nanostructure includes a free-standing semiconductor

10 oxide nanoring. The nanoring has a radius of about 500 to 10,000 nanometers, a height

of about 5 to 2000 nanometers, and a width of about 50 to 7500 nanometers.

This disclosure also involves a method of preparing nanostructures. A

representative method includes: providing a homogeneous metal oxide powder mixture;

exposing the homogeneous metal oxide powder mixture to thermal conditions of about

15 900 to 1600 °C at a pressure of about 10^{-3} to 10^{-2} torr for about 5 to 100 minutes; flowing

an inert gas over the homogeneous metal oxide powder mixture; and forming a free-

standing semiconductor oxide nanostructure via a condensation reaction at a pressure of

about 50 to 800 torr at thermal conditions of about 100 to 700 °C, each of the free-

standing semiconductor oxide nanostructures having a substantially rectangular cross-

20 section.

Other systems, methods, features, and advantages of this disclosure will be or

become apparent to one with skill in the art upon examination of the following drawings

and detailed description. It is intended that all such additional systems, methods, features,

and advantages be included within this description, be within the scope of this disclosure, and be protected by the accompanying claims.

BRIEF DESCRIPTION OF THE DRAWINGS

5   Many aspects of this disclosure can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, emphasis instead being placed upon clearly illustrating the principles of this disclosure. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

10   FIG. 1 includes schematics that illustrate a perspective view, a top view, a side view, and, an end view of a nanobelt.

FIG. 2 includes schematics that illustrate a perspective view, a top view, a side view, and, an end view of a nanosheet.

FIG. 3 is a schematic that illustrates an apparatus that can be used to fabricate the

15   nanobelt and/or the nanosheet shown in FIGS. 1 and 2.

FIG. 4 is a flow diagram illustrating a representative method for fabricating nanostructures as shown in FIGS. 1 and 2.

FIG. 5 illustrates scanning electron microscope (SEM) images of the as-synthesized ZnO nanobelts.

20   FIGS. 6A through 6G illustrate the controlled growth of (0001) polar surface dominated ZnO nanobelts. FIG. 6A illustrates a low-magnification transmission electron microscope (TEM) images and the corresponding electron diffraction patterns recorded from the areas as indicated by a sequence number from a TEM grid without tilting,

showing their unanimous [0001] orientation on a flat carbon substrate. FIG. 6B

illustrates a TEM image and the corresponding electron diffraction pattern, showing that

the nanobelt grows along [$2\bar{1}\bar{1}0$] (a-axis), with ±(0001) top and bottom surfaces, and ±

($01\bar{1}0$) side surfaces. FIG. 6C illustrates a high-resolution TEM image recorded from the

5   center of the nanobelt given in FIG. 6B, showing its dislocation-free volume. The inset is

the projected model of the wurtzite ZnO along [0001]; the positions of the Zn atoms are

in correspondence to the white dots observed in the image. FIG. 6D illustrates a [0001]

profile high-resolution TEM image recorded from the edge of the nanobelt given in FIG.

6B, showing the flatness of the surface. FIG. 6E illustrates a low magnification TEM

10   image and the corresponding electron diffraction patterns recorded from the circled

regions, displaying the geometry of the nanobelt. The difference between the two electron

diffraction patterns is due to the bending in the local regions. The contrast observed in the

image is the bending contour in electron imaging produced by the deformation of atomic

planes. FIG. 6F illustrates a TEM image showing the helical twist of a nanobelt. The

15   dark contrast at the top is due to the local strain. FIG. 6G illustrates the structure model

of the ZnO nanobelt.

FIGS. 7A through 7D illustrate SEM images of the as-synthesized ZnO nanobelts,

showing helical nanostructure.

FIGS. 8A through 8E illustrate TEM images and the corresponding electron

20   diffraction patterns recorded from the regions marked in the figure from an incomplete

ring, a single-looped ring, double-looped ring, and multiple-looped ring, respectively,

without tilting the specimen. Enlarged images from the nanobelts are inserted, from

which the number of loops and the contact between the nanobelts can be directly imaged.

Electron diffraction patterns recorded from the nanorings unanimously prove that the

normal direction of the circular ring plane is [01$\bar{1}$0], and the [0001] c-axis is pointing to

the ring center and it rotates following the arc of the ring. Electron diffraction patterns

5   recorded from the straight nanobelts or substantially straight nanobelts are [0001] pattern.

FIG. E illustrates convergent beam electron diffraction from a nanobelt, showing the

polarity of the nanobelt as evidenced by the asymmetric intensity distribution in the

(0002) and (000$\bar{2}$) disks. The result shows that the interior of the nanoring is positive

charged and the exterior is negatively charged.

10   FIG. 9A illustrates a TEM image of a helical nanostructure formed by multiple-

loop rolling up of a nanobelt. FIG. 9B illustrates a schematic model showing the relative

orientation for recording high-resolution TEM images along the axial direction of the

helical nanostructure ([$\bar{1}$2$\bar{1}$0]), and the [01$\bar{1}$0] perpendicular to the nanobelt and parallel

to its polar surface. FIG. 9C illustrates a [$\bar{1}$2$\bar{1}$0] high-resolution TEM image of a

15   nanobelt showing the dislocation-free volume but with the presence of stacking faults

(SFs). FIG. 9D illustrates two possible atomic models in correspondence to the HRTEM

image given in FIG. 9C, showing that stacking fault has no effect on the polarity of the

nanobelt. FIG. 9E illustrates a [01$\bar{1}$0] high-resolution TEM image of a nanobelt and the

profile of its side surface, showing dislocation-free volume. FIG. 9F illustrates an

20   enlargement of the image given in FIG. 9E and the projected atomic structure model.

FIG. 10A illustrates a low-magnification SEM image of the as-synthesized ZnO

nanorings. FIGS. 10B through 10D illustrate high-magnification SEM images of

freestanding, single-crystal ZnO nanorings, showing substantially uniform geometrical shapes.

FIGS. 11A through 11I illustrate the structure of the type I ZnO single-crystal nanoring. FIG. 11A illustrates a TEM image of a ZnO nanoring viewed with the electron beam parallel to the plane of the nanoring, while (a_1) illustrates an electron diffraction pattern recorded from area a_1 marked in FIG. 11A, (a_2) illustrates an enlargement of area a_2 marked in (A), showing a loose end at the left-hand side, and (a_3) illustrates electron diffraction pattern recorded from the loose end (area a_3 marked in a_2). FIGS. 11B and 11C illustrate bright-field and dark-field TEM images recorded from the nanoring after tilting about 15°, while (b) illustrates electron diffraction pattern recorded from the area (b) marked in FIG. 11B. FIGS. 11D through 11F illustrate larger images from the areas (d, e, f), respectively, marked in FIG. 11A, after slightly tilting the nanoring. FIG. 11G illustrates an enlarged TEM image of the nanoring tilted about 10°. FIG. 11H illustrates an enlargement of the area h indicated in FIG. 11C, which shows a uniform distribution of stacking faults across the entire width of the nanoring. FIG. 11I illustrates a high-resolution TEM image recorded from the nanoring when the incident electron beam is parallel to the ring-plane, showing stacking faults inside the nanobelt and at the interface between the coiled loops.

FIGS. 12A through 12H illustrate the structure of the type II ZnO single-crystal nanoring. FIGS. 12A and 12B illustrate bright-field and dark-field TEM images, respectively, recorded from the nanoring with the incident electron beam parallel to the ring plane. FIG. 12C illustrates an electron diffraction pattern recorded from the nanoring. The pattern shows vertical mirror symmetry, and the extra diffraction spots at

the two sides are from the cylindrical bending of the single-crystal ribbon. FIG. 12D

illustrates a high-resolution TEM image recorded from the central symmetric line in FIG.

12A. FIGS. 12E and 12F illustrate enlarged TEM images from the areas (e) and (f)

marked in FIG. 12A, respectively, showing the coiling layers. FIGS. 12E and 12F

5   illustrate bright-field and dark-field TEM images recorded form the nanoring after tilting

about 15°.

FIG. 13A illustrates a structure model of ZnO and the corresponding crystal

planes showing the ±(0001) polar surfaces. FIGS. 13B through 13E illustrate proposed

growth processes and corresponding experimental results showing the initiation and

10   formation of the single-crystal nanoring via self-coiling of a polar nanobelt.

DETAILED DESCRIPTION

This disclosure describes free-standing nanostructures and methods of fabrication

thereof. In general, the free-standing nanostructures have substantially rectangular cross-

15   sections. Embodiments of the free-standing nanostructure may be defect free, dislocation

free, and/or structurally uniform, while the surfaces of the free-standing nanostructure are

specific crystallographic planes. In addition, the structure and the morphology of the

free-standing nanostructure can be controlled using embodiments of the method of

fabrication. In this manner, the free-standing nanostructures and methods of fabrication

20   thereof may overcome some of the deficiencies described above.

In general, the free-standing nanostructures can be nanobelts, nanosheets,

nanodiskettes, helical nanostructrues, or nanorings, that have a substantially rectangular

cross-section. FIG. 1 illustrates a perspective view (A), a top view (B), a side view (C),

and an end view (D) of a nanobelt 10. The perspective view (A) illustrates a top 12, a

side 14, and an end 16 of the nanobelt 10. The top view (B), side view (C), and the end

view (D) illustrate the top 12, the side 14, and the end 16 of the nanobelt 10. FIG. 2

illustrates a perspective view (A), a top view (B), a side view (C), and an end view (D) of

5   a nanosheet 20. The perspective view (A) illustrates a top 22, a side 24, and an end 26 of

the nanosheet 20. The top view (B), the side view (C), and the end view (D) illustrate the

top 22, the side 24, and the end 26 of the nanosheet 20.

Nanobelts 10 can be characterized as "ribbon-like" structures, while the

nanosheets 20 can take the form of a variety of polygonal shapes such as, for example, a

10   rectangle, a square, a triangle, *etc.* Nanodiskettes (not shown) are similar to nanosheets

20 except that nanodiskettes are "coin-shaped" structures. The structure of the helical

nanostructure (as shown in FIG. 5 in Example 1B) can be described as a nanobelt

configured as helix (*e.g.*, coil or ring structure) having a substantially uniform radius

along the length of the helix. The structure of the nanoring (as shown in FIG. 10 in

15   Example 1C) can be described as a plurality of contiguous side-by-side loops of a

nanobelt. This disclosure does not describe in any definite dimensions the difference

between nanobelts 10, nanosheets 20, and nanodiskettes. For clarity, this disclosure

refers to nanobelts, nanosheets, and nanodiskettes as "nanostructures," unless the

structure being referred to is specifically denoted as a nanobelt, a nanosheet, a

20   nanodiskette, a helical nanostructure, or a nanoring.

The nanostructures are fabricated of at least one semiconductor oxide and/or at

least one doped semiconductor oxide. The semiconductor oxide includes oxides of zinc,

cadmium, mercury, gallium, indium, tellurium, germanium, tin, and lead. The

nanostructure fabricated of at least one semiconductive oxide can be, for example, a binary or a ternary complex of the semiconductor oxide.

The doped semiconductor oxide includes at least one semiconductive oxide that can be doped with at least one dopant that may be chosen from aluminum, gallium,

5   boron, yttrium, indium, scandium, silicon, germanium, titanium, zirconium, hafnium, antimony, tin, nitrogen, and fluorine. The nanostructure can be fabricated of at least one doped semiconductor oxide, for example, a binary or a ternary complex of the doped semiconductor oxide.

The size (*e.g.*, length, width, and height (thickness)) of the nanostructure can vary

10   within a type of semiconductor oxide and among each of the semiconductor oxides. The size of the nanostructure can be controlled to fit certain criteria for a particular application. However, in general, the nanostructures can be about 20 nanometers to about 6000 nanometers in width, about 5 nanometers to about 100 nanometers in height, and about 100 nanometers to about 3 millimeters in length. The nanostructures can have a

15   width-to-height ratio of about 5 to about 15. In addition to the dimensions described above, the following examples describe illustrative sizes of the nanostructures for some of the semiconductor oxides.

As mentioned above, the helical nanostructure includes a nanobelt having a substantially rectangular cross-section. In addition, the helical nanostructure is a single

20   crystalline structure. The radius of the helical nanostructure is about 200 nanometers to

      5000 nanometers, and specifically can be about 400 nanometers to 800 nanometers. The width of the nanobelt is about 5 nanometers to 200 nanometers, and specifically can be about 10 nanometers to 60 nanometers. The height of the nanobelt is about 3 nanometers

to about 50 nanometers, and specifically can be about 5 nanometers to 20 nanometers. The nanobelt is about 100 nanometers to 3 millimeters in length.

An exemplary embodiment of the helical nanostructure includes a helical zinc oxide nanostructure that includes a polar surface dominated zinc oxide nanobelt. The zinc oxide nanobelt includes polarized ±(0001) facets and, in particular, the zinc oxide nanobelt includes a top ±(0001) surface, a bottom ±(0001) surface, a right side ($10\bar{1}0$) surface, and a left side -($10\bar{1}0$) surface.

As mentioned above, the nanoring includes a nanobelt having a substantially rectangular cross-section. In addition, the nanoring is a single crystalline structure. The structure of the nanoring can be described as a plurality of contiguous side-by-side loops of the nanobelt. The dimensions of the nanobelt are similar to those described above for the helical nanobelt. The nanoring includes about 1 to 250 loops of the nanobelt, and suitably about 10 to 200 loops of the nanobelt. The nanoring has a radius of about 500 nanometers to 10,000 nanometers, and suitably about 600 nanometers to 2000 nanometers. The nanoring has a height of about 5 nanometers to 2000 nanometers, and suitably about 5 nanometers to 30 nanometers. The nanoring has a width of up to about 7500 nanometers, and suitably about 200 nanometers to 1000 nanometers.

An exemplary embodiment of the nanoring includes a polar surface dominated zinc oxide nanobelt. The zinc oxide nanobelt includes polarized ±(0001) facets and, in particular, the zinc oxide nanobelt has an interior (0001)-Zn surface and an exterior ±($000\bar{1}$)-O surface. The zinc oxide nanobelt includes a top ±(0001) surface, a bottom ±(0001) surface, a right side ($1\bar{2}10$) surface, and a left side -($1\bar{2}10$) surface.

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In general, the methods for fabricating nanostructures can be based on thermal evaporation of oxide powders under controlled conditions that can be performed on the apparatus 30 shown in FIG. 3. The apparatus 30 includes a horizontal tube furnace 32 that has an alumina tube 36 therein and is wrapped in a heating coil 34. Inside the alumina tube

5   36 are one or more alumina plates 38 and an alumina crucible 40, which contains the oxide powder 42 and/or other chemicals used to fabricate the nanostructures. To measure the temperature at various locations in the furnace 32, a thermocouple 44 or other temperature measuring device can be moved within the furnace 32. The apparatus 30 is also equipped with input 46 and output tubes 48 to introduce and pump-out a flow gas such as Argon .

10   (Ar). Additional features known by one skilled in the art are also included in the apparatus such as vacuum pumps, vacuum manifolds, reactant gas inputs, reactant gas manifolds, *etc.*, and will not be discussed here.

In practice, the desired oxide powder is placed in the aluminum crucible 40 in the center of an alumina tube 36. The temperature, pressure, and evaporation time are

15   controlled. Typically, the evaporation is performed without a catalyst. Except for the evaporation temperature that can be determined based on the melting point of the oxides used, the following parameters are typically kept constant: evaporation time (*e.g.*, 2 hours), alumina tube 36 pressure (*e.g.*, 300 Torr), and flow gas flow rate (*e.g.*, Argon flowed at approximately 50 standard cubic centimeter per minute (sccm)). During evaporation, the

20   products of the evaporation are deposited onto the alumina plates 38 located at the downstream end of the alumina tube 36.

Typically, the as-deposited products can be characterized and analyzed by x-ray diffraction (XRD) (Philips PW 1800 with Cu Kα radiation), scanning electron microscopy

(SEM) (Hitachi S800 FEG), transmission electron microscopy (TEM) (Hitachi HF-2000

FEG at 200 kV and JEOL 4000EX high resolution TEM (HRTEM) at 400 kV), and energy

dispersive x-ray spectroscopy (EDS).

Reference will now be made to the flow diagram of FIG. 4. FIG. 4 illustrates a

representative method of preparing a plurality of semiconductor oxide nanostructures

having a substantially rectangular cross-section from an oxide powder. Initially, the

oxide powder is heated to an evaporation temperature of the oxide powder for about 1

hour to about 3 hours at about 200 torr to about 400 torr in an atmosphere comprising an

inert gas such as Argon, as shown in block 42. Then, the oxide powder is evaporated, as

shown in block 44. Thereafter, the plurality of semiconductor oxide nanostructures is

formed, as shown in block 46.

In regard to helical nanostructures and nanorings, the following describes a

representative method for preparing helical nanostructures and nanorings. Additional

details for the method are described in reference to Examples 1B and 1C. Initially, a

metal oxide powder (*e.g.*, zinc oxide with a small amount of lithium oxide, indium oxide,

and/or lithium carbonate) is exposed to thermal conditions of about 900 to 1600°C (in

particular, about 1350 to 1400 °C) at a pressure of about 50 to 800 torr for about 5 to100

minutes (in particular, about 30 minutes). After the metal oxide powder is heated at a

pressure of about 10^{-3} to 10^{-2} torr, an inert gas, such as Argon, is flowed (*e.g.*, about 25 to

50 standard cubic centimeters per second) over the decomposing and evapoating metal

oxide powder. Subsequently, free-standing semiconductor oxide nanostructures (*e.g.*,

helical nanostructures and nanorings) are formed via a condensation reaction at a pressure

of about 50 to 800 torr (particularly, about 250 to 500 torr) at thermal conditions of about

100 to700°C (particularly, about 200 to 500 °C). The processing conditions can be adjusted to control the amount of each type of nanostructure formed as described below in Examples 1B and 1C.

Having summarized the nanostructures and methods of fabrication thereof above,

5   reference will now be made in detail to six illustrative examples of the semiconductor oxide nanostructures. While the invention is described in connection with these examples, there is no intent to limit the invention to the following examples. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of the invention.

10   Examples 1-4 are discussed in the following papers entitled "Nanobelts of Semiconducting Oxides," published in *Science* Vol. 291, 9, March 2001, "Spontaneous polarization induced nanohelicals, nanosprings, and nanorings of piezoelectric nanoblets," *(Nano Letters*, December 2003), and "Single-crystal cylindrical nanorings formed by epitaxial self-coiling of polar-nanoblets," *(Science*, in review), which are herein

15   incorporated by reference. Example 5 is discussed in the paper entitled "Gallium Oxide Nanoribbons and Nanosheets," and is in-press at the *Journal of Physical Chemistry B*, which is herein incorporated by reference. Example 6 is discussed in the paper entitled "Lead Oxide Nanobelts and Phase Transformation Induced by Electron Beam Irradiation," and is in-press at *Applied Physics Letters*, which is herein incorporated by reference.

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Example 1A: Zinc Oxide

Thermal evaporation of zinc oxide (ZnO) powders (purity: 99.99%, melting point: 1975 °C) at 1400 °C for approximately 2 hours resulted in white wool-like products that formed in high yield on the surface of the alumina plate 38. Scanning electron microscopy (SEM) observations reveal that the products consist of a large quantity of nanostructures

5   with typical lengths in the range of several tens to several hundreds of micrometers, while some of nanostructures have lengths on the order of millimeters. EDS microanalysis and powder XRD measurement show that the sample is wurtzite (hexagonal) structured ZnO with lattice constants of $a = 3.249$ Å and $c = 5.206$ Å, consistent with the standard values for bulk ZnO.

10   TEM images reveal that the ZnO nanostructure has a substantially rectangular cross-section (*i.e.*, nanobelt) that is distinct in cross-section from nanotubes and nanowires. Each nanobelt has a uniform width along a substantial portion of the length of the nanobelt, and the typical widths of the nanobelts are in the range of 50 to 300 nanometers. In addition, the ends of the nanobelts do not include a particle. The typical height and width-to-height

15   ratios of the ZnO nanobelts are in the range of 10 to 30 nanometers and about 5 to about 10, respectively. HRTEM and electron diffraction show that the ZnO nanobelts are structurally uniform and single crystalline but with two different growth directions. The nanobelt, growing along [0001] and enclosed by $\pm (2\bar{1}\bar{1}0)$ and $\pm (01\bar{1}0)$ facets, shows no defect and dislocations. The nanobelt, growing along $[01\bar{1}0]$ and enclosed by $\pm (0001)$ and

20      $\pm (2\bar{1}\bar{1}0)$ facets, is also dislocation free but with only a single stacking fault that is parallel to the axis and runs throughout the entire length of the nanobelt. The surfaces of these nanobelts are clean, atomically sharp, and without any sheathed amorphous phase.

Example 1B: Zinc Oxide

Zinc oxide (ZnO) is a versatile "smart" material that has applications in catalysts, sensors, piezoelectric transducers, transparent conductor, and surface acoustic wave devices. The non-central symmetry and the tetrahedrally coordinated ZnO_4 unit in ZnO result in anisotropic piezoelectric properties. Structurally, the wurtzite structured

5   ZnO crystal is described schematically as a number of alternating planes composed of fourfold coordinated O^{2-} and Zn^{2+} ions, stacked alternatively along the c-axis. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (000$\bar{1}$)-O polar surfaces, resulting in a normal dipole moment and spontaneous polarization, as well as a divergence in surface energy. To maintain a stable structure, the

10   polar surfaces generally have facets or exhibit massive surface reconstructions, but ZnO ±(0001) is an exception, which is atomically flat, stable, and without reconstruction.

Nanowire and nanotube based materials have been demonstrated as building blocks for nanocircuits, nanosystems, and nano-optoelectronics and they have been fabricated for a wide range of materials including, for example, metals, semiconductors,

15   oxides, and polymers. A variety of quasi-one-dimensional ZnO nanostructures, such as nanowires and nanobelts, have been synthesized, and they have been used for fabricating nano-scale lasers, field effect transistors, gas sensors, cantilevers, and resonators. But these ZnO nanostructures grow along the c-axis and the side surfaces are {01$\bar{1}$0} and {2$\bar{1}$$\bar{1}$0}, due to their lower energies than that of (0001), resulting in vanishing dipole

20   moment and much reduced piezoelectricity. The most desirable morphology to maximize the piezoelectric effect is to create nanostructures that preserve large area (0001) polar surfaces. However, ZnO (0001) has a surface energy that diverges with sample size due

to the surface polarization charge. Therefore, growth of (0001) surface dominated

freestanding nanostructures needs to overcome the barrier of surface energy.

As described in this disclosure, it was found that the freestanding ZnO nanobelts

that grow along the a-axis and their large top and bottom surfaces are the polar (0001)

5   facets. Due to the small thickness of the nanobelts, spontaneous polarization normal to

the nanobelt leads to the growth of helical nanostructures. The mechanism for the helical

growth is attributed to a consequence of minimizing the total energy contributed by

spontaneous polarization and elasticity. The ZnO nanostructures have potential

applications as nano-scale sensors, resonators, and transducers that can serve as

10   functional components to be integrated in micro- and nano-electromechanical systems

(MEMS, NEMS). They are also ideal systems for understanding piezoelectric effect and

spontaneous polarization induced ferroelectric effect at nano-scale.

The structurally controlled, high purity, and high yield ZnO nanobelts were

synthesized by a solid-vapor process. A homogeneous mixture of zinc oxide powder

15   (purity 99.99%, melting point 1975 °C) and 1 weight % of lithium oxide (or indium

oxide) were placed at the highest temperature zone of a horizontal tube furnace. Before

heating to the desired temperature of about 1420°C (1360 °C when using indium oxide),

the tube furnace was evacuated to about 10^{-2} torr to remove the residual oxygen. Then

the source materials were heated to about 1420°C at a heating rate of about 20°C/min.

20   ZnO decomposes into Zn^{2+} and O^{2-} at high temperatures (about 1350°C) and low

pressures (about 10^{-3} torr). This decomposition process can be used to control the

anisotropic growth of the nanobelts. After a few minutes of evaporation and

decomposition, the Ar carrier gas was introduced at a flux of about 25 sccm (standard

cubic centimeters per minute) which kept the pressure at about 200 torr. The synthesis process was conducted at about 1350 °C for about 30 minutes. The nanobelts were deposited onto an alumina substrate placed in a temperature zone of about 400 to 500°C under Ar pressure of about 200 torr. Structures of the ZnO nanobelts were analyzed by

5   scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM).

SEM and TEM analysis shows that the as-prepared product has a belt-shape with widths of about 10 to 60 nanometers (nm), thickness of about 5 to 20 nm and lengths up to about several hundred micrometers. The dominant component of the as-synthesized

10   sample is nanobelts with a uniform size distribution, but a significant amount of nanobelts have a ring shape (nanorings) (as indicated by arrowheads in FIG. 5), which has not been found for single-crystal nanobelts or nanowires of any other materials.

The ZnO nanobelt has a controlled structure. By examining over a hundred of nanobelts laid down naturally onto a carbon film by electron diffraction (ED), more than

15   90% of them demonstrated the same orientation of [0001] with respect to the incident electron beam (FIG. 6A), indicating that the top flat surfaces of the nanobelts are the polar $\pm(0001)$ facets. This clearly demonstrates the success of overcoming the surface energy barrier by growth kinetics in order to achieve structural control. The ZnO nanobelt has a wurtzite structure with lattice constants of $a = 0.325$ nm and $c = 0.521$ nm.

20   Indexing of the ED pattern shows that the nanobelt grows along $[2\bar{1}\bar{1}0]$ (the a-axis), with its top/bottom surface $\pm(0001)$ and the side surfaces $\pm (01\bar{1}0)$ (FIG. 6B). HRTEM shows that the nanobelt is single crystalline without the presence of dislocations (FIG. 6C), and

its geometrical shape is uniform. The surfaces of the nanobelt are clean, atomically sharp

and flat (FIG. 6D). Due to the small thickness of about 5 to 20 nm and large aspect ratio

of about 1:4, the flexibility and toughness of the nanobelts are both extremely high so that

they can be bent or twisted without fracture (FIGS. 6E and 6F). The crystallographic

5   structural model of an exemplary nanobelt is illustrated in FIG. 6G.

Besides a significant portion of nanorings observed in FIG. 5, the most striking

feature of the sample is the formation of helical structures by rolling up single crystalline

nanobelts (FIGS. 7A through 7D). The helical nanostructure has a uniform shape with

radii of about 500 to 800 nm and evenly distributed pitches. A nearly perfect circular arc

10   is formed by a single nanobelt (FIG. 8A). Electron diffraction indicates that the direction

of the radius toward the center of the ring is always [0001] along the entire perimeter

without significant twisting, and the circular plane of the nanoring is $[01\bar{1}0]$. A full

circular ring formed by a closed nanobelt shows a consistent orientation (FIG. 8B); the

orientation of the straight or nearly straight nanobelts are along [0001], consistent with

15   the result from FIG. 6A. The orientation relationship illustrated in FIG. 8A is preserved

for nanorings formed by double-looped FIG. 8C and multiple-looped FIG. 8D rolling of a

nanobelt. The orientation of the two wider nanobelts across the nanoring in FIG. 8C is

[0001]. The enlarged images from the double-looped ring in FIG. 8C clearly indicate that

the two loops of the nanobelt are in physical contact and there is even a small gap (about

20   1 to 2 nm, see the insets in FIG. 8C) between them, suggesting that the interaction

between the loops is weak and there is no chemical bonding. Overlap among the loops is

possible for multiple-looped ring (see the inset in (FIG. 8D).

The (0001) plane can be terminated with Zn [(0001)-Zn] or oxygen [(000$\bar{1}$)-O], resulting in positively and negatively charged top and bottom surfaces, respectively. Convergent beam electron diffraction has been applied to determine the polarity (FIG. 8E), and the result indicates that the interior surface of the ring is (0001)-Zn and the

5   exterior surface is (000$\bar{1}$)-O. Physically, if the surface charges are uncompensated during the growth, the net dipole moment tends to diverge and the electrostatic energy increases. For a thin nanobelt laying on a substrate, the spontaneous polarization induces electrostatic energy due to the dipole moment, but rolling up to form a circular ring would minimize or neutralize the overall dipole moment, reducing the electrostatic energy. On

10   the other hand, bending of the nanobelt produces elastic energy. The stable shape of the nanobelt is determined by the minimization of the total energy contributed by spontaneous polarization and elasticity.

The atomic structure of the nanobelt has been investigated by HRTEM. The model for the helical nanostructure shown in FIG. 9A is given in FIG. 9B. Two

15   orientations have been selected to investigate the atomic structure of the helical nanostructure. The first orientation is along the axis of the helical nanostructure, which is [$\bar{1}$2$\bar{1}$0], and the second orientation [01$\bar{1}$0] is parallel to the top (0001) surface and perpendicular to the side surface of the nanobelt. The HRTEM image recorded along [$\bar{1}$2$\bar{1}$0] shows clearly the (10$\bar{1}$0) (d = 0.28 nm) and (0002) (d = 0.26 nm) fringes without

20   the presence of dislocation, but stacking faults parallel to the (0001) plane are identified. The stacking fault is extrinsic with insertion of an extra Zn-O layer parallel to the basal plane. It should be noted that the presence of (0001) stacking faults does not affect the

polarity of ZnO, as shown by the models in FIG. 9D. The HRTEM image recorded along

[01$\bar{1}$0] clearly presents the (0002) (d = 0.26 nm) and (2$\bar{1}$ $\bar{1}$ 0) (d = 0.16 nm) fringes (FIG.

9E). An enlarged image and the projected atomic structural model are shown in FIG. 9F,

which also preserves the polarity. The top surface of the nanobelt is flat with the

presence of a few atom-height steps as displayed by the profile image in FIG. 9E.

The growth of polar facets dominated nanobelt surfaces is a major step towards

development of piezoelectric and ferroelectric one-dimensional nanostructures. Since the

ZnO (2$\bar{1}$ $\bar{1}$ 0) plane has a surface energy lower than that of either (0001) or (01$\bar{1}$0), a fast

growth along [2$\bar{1}$ $\bar{1}$ 0] (a-axis) to form a nanobelt structure may be unfavorable from the

energy point of view. But the success of controlled growth of free-standing (0001) polar

surface dominated nanobelts along the a-axis demonstrates the experimental feasibility of

overcoming the energy barrier through growth kinetics, thus, providing a feasible

approach for growing structurally controlled nanobelts of technological importance.

Helical structure is the most fundamental structural configuration for DNA and

many biological proteins, which is due to van der Waals forces and hydrogen bonding. For

one-dimensional nanostructures, nanocoils, and nanorings have been observed for carbon

nanotubes and SiC, the former are created due to a periodic arrangement of the paired

pentagon and heptagon carbon rings in the hexagonal carbon network, and the latter are due

to a stacking of platelets around the growth axis. These helical structures are produced by

the presence of point or planar defects (twins and stacking faults). A difference for the

helical nanostructures for single crystalline ZnO nanobelt described here is that they are the

spontaneous polarization induced structures. The nanobelts and helical nanostructures are

an ideal system for understanding piezoelectricity and polarization induced ferroelectricity at nano-scale.

Example 1C: Zinc Oxide

Self-assembly is a fundamental approach for organizing and constructing
5   hierarchical structures using nano-building-blocks through substrate patterning and surface functionalization. Self-assembly of nanocrystals is driven by van der Walls forces and hydrogen bonding among the passivating organic molecules on the particle surfaces. Polar-charge induced self-assembly is frequently observed for chain molecules in a solution environment: a local spontaneous ordering of molecular polarity and chirality
10   resulting in the formation of stripes; and chiral domains of achiral molecules and ferroelectric liquid crystals being polarization-induced self-assembly. For crystalline nanomaterials grown in a solid-vapor environment, one type of polar-charge induced helical and spiral structures of ZnO has been done (see Example 1B). In this example, a distinct and unique nanoring structure that is formed by spontaneous self-coiling of a
15   polar nanobelt during growth is described. Although not intending to be bound by theory, the nanoring is suggested to be initiated by circularly folding a nanobelt due to long-range electrostatic interaction, and the short-range chemical bonding among the loops leads to a single-crystalline structure. The self-coiling is driven by minimizing the energy contributed by polar charges, surface area, and elastic deformation.

20   The single-crystal nanorings of ZnO were grown at a high reproducibility by a solid-vapor process. A homogeneous mixture of ZnO powder (melting point 1975 °C) and indium oxide and lithium carbonate at about a 20:1:1 ratio were positioned at the highest temperature zone of a horizontal tube furnace. Before heating to a desired

temperature of about 1400°C, the tube furnace was evacuated to about 10^{-3} torr to remove

the residual oxygen. The source materials were then heated to about 1400 °C at a heating

rate of about 20°C/min. ZnO decomposes into Zn^{2+} and O^{2-} at high temperature (about

1400°C) and low pressure (about 10^{-3} torr), and this decomposition process can be used to

5   control the anisotropic growth of the nanobelts. After a few minutes of evaporation and

decomposition, the Ar carrier gas was introduced at a flux of about 50 sccm to maintain

the pressure at about 500 torr for about 30 minutes. The synthesis process was conducted

at about 1400 °C for about 30 minutes. The condensation products were deposited onto a

silicon substrate placed in a temperature zone of about 200 to 400°C under Ar pressure of

10   about 500 torr. The as-synthesized samples were analyzed by SEM and HRTEM.

The as-synthesized sample is composed of a plurality of freestanding nanorings

at a percentage of about 20 to 40% (FIG. 10A), with typical diameters about 1 to 4 μm,

thin and wide shells of thicknesses about 10 to 30 nm. SEM images recorded at high-

magnification illustrate the perfect circular shape of the complete rings, with uniform

15   shape and flat surfaces (FIG. 10B through 10D). Energy dispersive X-ray spectroscopy

analysis indicates that the nanorings are ZnO.

Two types of nanoring structures have been found. The type I structure is

illustrated in FIG. 11A through 11I. TEM image (FIG. 11A) indicates that the nanoring is

a single-crystal entity with nearly perfect circular shape, although there is diffraction

20   contrast due to non-uniform deformation along the circumference. The single-crystal

structure referred here means a complete nanoring that is made of a single crystalline

ribbon bent evenly at the curvature of the nanoring. Tilting the nanoring for about 20°

clearly illustratess the single-crystal circular shape (FIG. 11B). The corresponding dark-

field TEM image (FIG. 11C) shows the contrast produced by the equal bending lines across the width of the nanoring (FIG. 11C), which is due to the tilting of the atomic plane with respect to the electron beam. Deformation in the nanometer-thickness ribbon does not need to introduce dislocations. An electron diffraction pattern recorded from the

5   center of the nanoring (area a_1 indicated in FIG. 11A) shows that the radial direction of

the nanoring is [1 $\bar{2}$ 10], tangential direction [10$\bar{1}$0] and nanoring axis [0001] (the model for these planes and directions are given in FIG. 13A). High-magnification TEM image recorded from the three corners of the image presented in FIG. 11A (areas d, e and f) are shown in FIGS. 11D through 11F, respectively, which clearly illustrate the distribution of

10   the equally spaced stacking faults nearly parallel to the nanoring plane. The stacking faults align from the top of the nanoring to the bottom without interruption (FIGS. 11D and 11F). The trace of the coiling nanobelt is best illustrated through the side of the nanoring, as indicated by arrowheads in FIG. 11F. The entire nanoring is a single crystal, although the quality of the crystallinity varies slightly across the width of the nanoring, as

15   presented by the enlarged TEM image in FIG. 11G.

The nanoring is made of co-axial, uni-radius, and epitaxial-coiling of a nanobelt. By carefully examining the image given in FIG. 11A, a loose end of the raveling nanobelt is found, as indicated by a red arrowhead. The coiling of this nanobelt to form the nanoring is presented by the enlarged image in FIG. 11F, as marked by an arrowhead at

20   the top. Examination of the other side of the nanoring found the other loose end of the nanobelt (as indicated by an arrowhead in FIG. 11E). Electron diffraction pattern recorded from the loose end of the nanobelt, as circled in the enlarged area a_3, indicates

that the nanobelt has a growth direction of $[10\bar{1}0]$, side surfaces $\pm(1\bar{2}10)$, and top/bottom

surfaces $\pm(0001)$. It is apparent that the nanoring is made of coiling loops of the

nanobelt, as in a child's "slinky" spring, by interfacing its (0001)-Zn and $(000\bar{1})$-O planes

at the same crystallographic orientation. The coiling of the nanobelt introduces a small

5   helical angle of about $0.3°$; this small rotation is hardly detectable by the electron

diffraction pattern.

The loose end of the nanobelt in FIG. 11F has a stacking fault at close to the

middle of its width, suggesting that the planar defect was produced during the nanobelt

growth and it is the key for leading to the fastest growth of the nanobelt along its axial

10   direction. The total number of coiling loops can be counted from the dark-field TEM

image displayed in FIG. 11H as being 33. High-resolution TEM indicates that, besides

the stacking fault inside the nanobelt, a stacking fault of a different type is formed at the

interface between the adjacent loops, which is introduced to match the lattices of the Zn-

terminated and the oxygen-terminated (0001) polar surfaces. The interface between the

15   loops is coherent, epitaxial, and chemically bonded (FIG. 11I).

The type II nanoring structure is illustrated in FIG. 12A through 12H. Bright-field

(FIG. 12A) and dark-field (FIG. 12B) TEM images unambiguously prove the single-

crystal structure of the complete nanoring, which again implies that the nanoring shell is a

uniformly-deformed single-crystal ribbon around the circumference. Electron diffraction

20   (FIG. 12C) and the corresponding high-resolution TEM image recorded from the central

region (FIG. 12D) show that the radial direction of the nanoring is $[1\bar{2}1\bar{3}]$, tangential

direction $[10\bar{1}0]$ and nanoring plane $(1\bar{2}12)$ (see the model in (FIG. 13A)), and there is

no dislocation in the volume. FIGS. 12E and 12F display the enlarged view of the two

corners indicated in FIG. 12A, which shows an end of the nanobelt (indicated by an

arrowhead) and the screw coiling of the nanobelt. The pitch distance for the coiling is

about 10 nm and the total number of loops is 100. The contrast produced by stacking

5   faults parallel to the nanoring plane is visible, but the (0001) stacking fault plane is at an

angle of about $28°$ from the nanoring axis. The nanoring has a thin crystal wall of

thickness about 15 nm, as illustrated by tilting the nanoring for $15°$ (FIGS. 12G and 12H).

The growth of the nanoring structures can be understood from the polar surfaces

of the ZnO nanobelt. The wurtzite structured ZnO crystal is described schematically as a

10   number of alternating planes composed of tetrahedral coordinated O^{2-} and Zn^{2+} ions,

stacked alternatively along the c-axis (FIG. 13A). The oppositely charged ions produce

positively charged (0001)-Zn and negatively charged $(000\bar{1})$-O polar surfaces. The polar-

nanobelt, which is the building block of the nanoring, grows along $[10\bar{1}0]$, with side

surfaces $\pm(1\,\bar{2}\,10)$ and top/bottom surfaces $\pm(0001)$, and have a typical width of about 15

15   nm and thickness about 10 nm.

The stacking fault parallel to (0001) lowers the nanobelt energy and is the key for

leading to the fastest anisotropic growth along $[10\bar{1}0]$, but it does not affect the intrinsic

polarity of the nanobelt. Therefore, the nanobelt has polar charges on its top and bottom

surfaces (FIG. 13B). If the surface charges are uncompensated during growth, the

20   nanobelt may tend to fold itself as its length increases in order to minimize the area of the

polar surface. Although not intending to be bound by theory, one possible way of folding

is to interface the positively charged (0001)-Zn plane (top surface) with the negatively

charged (0001)-O plane (bottom surface), resulting in neutralization of the local polar

charges and the reduced surface area, thus forming a loop with an overlapped end (as

shown in (FIG. 13B)). The radius of the loop may be a result of how the nanobelt folds at

the initial growth, but the size of the loop cannot be small to reduce the elastic

5   deformation energy. Although not intending to be bound by theory, calculations show

that the diameter should be no less than about 600 nm, and the experimental data show a

low limit of about 800 nm. However, embodiments of the nanoring may have a diameter

less than 600 nm. The total energy involved in the process coming from polar charges,

surface area, and elastic deformation. The long-range electrostatic interaction is likely to

10   be the initial driving force for folding the nanobelt to form the first loop for the

subsequent growth, as suggested by calculations. From the SEM images, it is submitted

that the first step (FIG. 13B) occurs before the nanoring landed onto the substrate.

       The presence of a stacking fault within the nanobelt (see FIG. 11F) is the key for

leading to the fast growth of the nanobelt along $[10\bar{1}0]$, because it lowers the energy in

15   the wurtzite-structured lattice. Although not intending to be bound by theory, as the

growth continues, the nanobelt may be naturally attracted onto the rim of the nanoring

due to electrostatic interaction and extends parallel to the rim of the nanoring to neutralize

the local polar charge and reduce the surface area, resulting in the formation of a self-

coiled, co-axial, uni-radius, multi-looped nanoring structure (FIG. 13C). The self-

20   assembly is spontaneous, which means that the self-coiling along the rim proceeds as the

nanobelt grows. The reduced surface area and the formation of chemical bonds (short-

range force) between the loops stabilize the coiled structure. The width of the nanoring

increases as more loops winding along the nanoring axis (FIG. 13D), and all of them

remain in the same crystal orientation. Since the growth was carried out in a temperature region of about 200-400 °C, "epitaxial sintering" of the adjacent loops forms a single-crystal cylindrical nanoring structure, and the loops of the nanobelt are joined by chemical bonds as a single entity. The loops that were coiled first remained at growth temperature

5   for a longer time, resulting in higher crystallinity, while the ones that wound on later had less time for sintering and thus had relatively poorer crystallinity, forming the structure illustrated in FIG. 11G with two contrast regions across the width of the nanoring. Finally, as the growth time was extended, the entire nanoring exhibits a high quality crystallinity, as illustrated by the diffraction contrast observed in FIG. 13E. A uni-radius

10   and perfectly aligned coiling is energetically favorable because of the complete neutralization of the local polar charges inside the nanoring and the reduced surface area. The entire growth process may have no relationship with the substrate used for collecting the sample.

The coiling process illustrated in FIGS. 13A through 13H unifies the two types of

15   nanoring structures described in FIG. 11A through 11I and 12A through 12H. If the (0001) polar surface of the ZnO nanobelt is parallel to the ring-plane, self-coiling of the nanobelt at a radial direction of [1 $\bar{2}$ 10] forms the type I structure presented in FIG. 11A through 11I. Alternatively, if the nanobelt is tilted towards the nanoring center so that the radial direction is [1 $\bar{2}$ 1 $\bar{3}$], self-coiling of the nanobelt produces the type II structure

20   presented in FIGS. 2A through 12H. The tilting of the nanobelt may reduce the elastic deformation energy.

The model discussed here can also be adopted to explain the helical nanostructure discussed above. If the nanobelt in FIG. 13B is alternatively flipped for 90° so that the radial direction of the nanoring is [0001], which means that the polarization is in the radial direction, a bending of the nanobelt into a circle slightly reduces the electrostatic energy, possibly in favor of forming an in-plane spiral nanoring. Alternatively, as a result of preserved polar charges on the inner and outer arc surfaces, the circular loops of the nanobelt of the same diameter cannot be densely packed into a single-crystal coil structure due to electrostatic repulsion among them; instead, a helix structure would be formed with a pitch distance of about 200-500 nm (much larger than the width (about 20 nm) or thickness (about 10 nm) of the nanobelt), which is suggested to be a result of balancing the electrostatic repulsive force between the loops and the elastic deformation force.

The polar-charge induced nanorings presented here have potential applications in investigating fundamental physical phenomena, such as the Aharonov-Bohm oscillations in the exciton luminescence. The unique piezoelectric and semiconducting properties of ZnO predict that the nanorings could be nano-scale sensors, transducers, and/or resonators.

Example 2: Tin Oxide

Single crystalline SnO_2 nanobelts of rutile structure can be fabricated by thermal evaporation of either SnO_2 powders (purity: 99.9%, melting point: 1630 °C) at 1350 °C and/or SnO powders (purity: 99.9%, melting point: 1080 °C) at 1000 °C. After evaporation, white fuzz-like products are deposited on the alumina plate 38, whether the source material was SnO_2 or SnO. SEM imaging and EDS analysis show that the products

are composed of large quantities of SnO_2 nanobelts (with lengths up to the order of millimeters) and a small fraction of Sn nanoparticles. XRD patterns from the synthesized SnO_2 nanobelt samples prove the rutile type structure with lattice constants of a = 4.722 Å and c = 3.184 Å, which are consistent with those of bulk SnO_2. TEM images display the

5   characteristic shape (e.g. rectangular cross-section) of the SnO_2 nanobelts. Each nanobelt is uniform in width and height, and the typical widths of the SnO_2 nanobelts are in the range of about 50 to about 200 nanometers. Cross-sectional TEM observations show that the cross-sections of the SnO_2 nanobelts are substantially rectangular, with typical width-to-height ratios of about 5 to about 10. High-resolution TEM images reveal that the nanobelts

10   are single crystalline and dislocation free. Electron diffraction pattern indicates that the SnO_2 nanobelt grows along [101], and it is enclosed by $\pm(010)$ and $\pm(10\bar{1})$ crystallographic surfaces.

Example 3: Indium Oxide

      Thermal evaporation of indium oxide (In_2O_3) powders (purity: 99.99%, melting

15   point: ~1920 °C) at 1400 °C yields In_2O_3 nanobelts. TEM observations show that most of the In_2O_3 nanobelts have uniform width and height along their lengths. However, some nanobelts exhibit a sharp shrinkage in width while the height is preserved and form a bridge-like structure, which may be used to measure transport from an oxide nanobridge. Typically, the In_2O_3 nanobelts have widths in the range of about 50 to about 150

20   nanometers and lengths of several tens to several hundreds of micrometers. Electron diffraction analysis shows that the In_2O_3 nanobelts are single crystalline, and grow along [001], the surfaces being enclosed by (100) and (010) surfaces.

Example 4: Cadmium Oxide

Nanobelts of cadmium oxide (CdO) with sodium chloride (NaCl) cubic structure can be fabricated by evaporating (CdO) powders (purity: 99.998%, melting point: 1430 °C) at 1000 °C. Besides CdO nanobelts, many single crystalline CdO sheets with sizes on the order of several to several tens of micrometers are also formed. These CdO sheets usually

5   have shapes such as rectangles, triangles, and parallelograms. The lengths of the CdO nanobelts are usually less than about 100 micormeters, and their widths are typically about 100 to about 500 nanometers, significantly wider and shorter than those of ZnO, SnO_2 and In_2O_3 nanobelts, respectively. As a result, the width-to-height ratios of CdO nanobelts are usually greater than 10. Electron diffraction pattern shows that the nanobelts grow along

10   [100], and their surfaces are enclosed by ±(001) and ±(010) facets. In addition, some nanobelts were broken into two halves during TEM observation due to electron beam illumination, which is likely to be caused by the easy cracking characteristic of the NaCl-type ionic structure of the nanobelt. Thus, it may be possible to cut these nanobelts with a focused electron or ion beam, so that nanobelts with specific lengths for nano-device

15   applications could be fabricated.

Example 5: Gallium Oxide

The synthesis of gallium oxide (Ga_2O_3) is based on thermal evaporation of gallium nitride (GaN) powders under controlled conditions in the presence of oxygen. The commercially supplied GaN powders (99.99% metals basis) are placed at the center of an

20   alumina tube 36. The furnace is heated at a rate of about 10-15 °C/min to about 1100 °C, and then maintained at this temperature for 2 hours before cooled down to room temperature. The pressure in the alumina tube 36 is about 300 Torr, and the Ar flow rate is about 50 sccm. During evaporation, the products are deposited onto alumina plates 38,

where the temperature is about 800-850 °C. The as-deposited products are wool-like with a light gray color.

SEM analysis reveals that the products consist of a large quantity of nanostructures with typical lengths in the range of several tens to several hundreds of micrometers, while some of the nanostructures have lengths on the order of millimeters. The as-synthesized sample also contains a large fraction of nanosheets, and size of the nanosheets is about 10 micrometers across and several tens of nanometers in height. The nanosheets have straight edges with sharp corners, suggesting that they terminate by faceted crystallographic planes. Chemical microanalysis using EDS shows that the nanostructures obtained are Ga_2O_3. The formation of Ga_2O_3 rather than GaN is believed due to the high combinability of Ga with oxygen, which is believed to leak into the furnace.

The width of the nanobelts varies from about 40 to about 300 nanometers, and the geometry of the nanobelts is substantailly uniform. The height of the nanobelts is about 10 to about 60 nanometers depending on the width. The nanobelts are single crystalline and free from dislocations. Their surfaces are clean without an amorphous layer.

Ga_2O_3 is of polymorphism in its crystal structure. The polymorph of Ga_2O_3 mainly includes α- ($R\bar{3}m$, a = 4.979 Å and c = 13.429 Å), β- ($C2/m$, a = 12.23 Å, b = 3.04 Å, c = 5.80 Å, and β = 103.7 Å) and γ-Ga_2O_3 ($Fd\bar{3}m$, a = 8.22 Å). Of those phases, the β-Ga_2O_3 is only stable modification. Some of the nanobelts are enclosed by $\pm$(100) top and bottom surfaces and $\pm$(10$\bar{1}$) side surfaces, while other nanobelts can be enclosed by $\pm$(201) top and bottom surfaces and $\pm$(010) side surfaces. It has been found that both the $\pm$(010) and the $\pm$(10$\bar{1}$) crystal planes can serve as the growth front of nanobelts with growth directions of

[010] and [001], respectively. The growth front of the nanoribbon is ±(010) and the

corresponding HRTEM image indicates a perfect crystallinity of the Ga_2O_3 nanobelt.

Nanosheets have some straight edges with corners of specific angles, typically of

45° and 90°. Some of the nanosheets are directly connected to nanobelts, indicating that

5 they have the same structure. Electron diffraction shows that the nanosheets have the same

crystal structure of β-Ga_2O_3 as that of nanobelts. The electron diffraction pattern

demonstrates the corresponding [101] crystal zone of β-Ga_2O_3. The two perpendicular

planes result in the rectangular- and L-shape structures. Beside the ±(010) and the

±(10$\bar{1}$) facets, a third-type of plane with about a 45° angle with respect to the two sides is

10 also observed. This type of plane is identified to be the (21$\bar{2}$) plane from the electron

diffraction pattern. The top and bottom surfaces are also the ±(100) crystal planes of β-

Ga_2O_3. Based on our SEM observation, the height of the nanobelts and nanosheets are

about 20-60 nanometers.

The growth morphology of Ga_2O_3 nanobelts and nanosheets is distinctively

15 different from that of Ga_2O_3 nanorods and nanowires. The nanorods grown by thermal

evaporation of a mixture of GaN, graphite and Ni particles have diameters of 5-10

nanobelts and growth directions of either [111] or [200]. The nanowires grown by an arc-

discharge of GaN with the presence of Co and Ni particles have diameters of 20-30

nanobelts and a growth direction of [001]. The formation of nanobelts and nanosheets is a

20 combined result of vapor-liquid-solid (VLS) and solid-solid (SS) growth kinetics.

Example 6

Thermal evaporation of lead oxide (PbO) powders (purity: 99.99%) at about 950°C yields PbO nanobelts. The thermal evaporation is conducted at 950 °C for 1 hour under a pressure of 300 Torr and Ar flowing at a flow rate of 50 sccm. The products deposited on the surface of the alumina plate 38 substrates are characterized by SEM, 5   TEM, and EDS.

The as-synthesized products display a dark gray color that is distinctive from the yellow colored PbO source powders. SEM observations reveal that the products consist of a large quantity of belt-like nanostructures and faceted particles with diameters in the range of about 0.1 to about 2 micrometers. Chemical analysis by EDS indicates that the 10   nanostructures are PbO_2 and the particles are metal Pb covered with a thin oxide layer.

TEM images show the morphology to be consistent with nanobelt morphology. The PbO_2 nanobelts are several tens to several hundreds of micrometers in length. Each nanobelt has a uniform width over its entire length, and the typical width of the nanobelts in the range of about 50 to about 300 nanometers. The height of the nanobelts varies with 15   its width, and typically is in the range of about 10 to about 30 nanometers, as estimated by TEM observations. The width-to-height ratio of the nanobelts is about 5 to about 10.

It is noted that each nanobelt is connected with a Pb particle at its growth front, implying that the Pb tip likely acts as a catalyst in growth of the nanobelt. The diameter of the Pb tips is several times bigger than the width of connecting nanobelts. The Pb tips 20   have the faceted geometrical shape of an octagonal projection, which indicates that Pb tips are crystalline and likely adopt the shape of truncated octahedron enclosed by (100) and (111) crystal planes because of lower surface energies.

PbO$_2$ can form two possible crystal structures (α and β) of orthorhombic and tetragonal lattice, respectively. Electron diffraction analysis and high resolution TEM imaging indicate that the as-synthesized PbO$_2$ nanobelt is single crystalline structure without dislocation and has a tetragonal structure (*P4/mnm*, a = 4.961 Å and c = 3.385

5   Å), *i.e.* β-PbO$_2$ nanobelts are formed. The nanobelt is enclosed by top surfaces $\pm$(201) and side surfaces $\pm$(10$\overline{1}$). The growth direction of the nanobelt is parallel to [010] with growth front (010).

The growth characteristics of the PbO$_2$ nanobelts is quite different from that of ZnO, SnO$_2$, In$_2$O$_3$, CdO and Ga$_2$O$_3$ nanobelts, in which no particle was found at the

10   growth fronts of the nanobelts. This implies that a different growth mechanism be employed by the PbO$_2$ nanobelts. The growth of the former five oxide nanobelts may be governed by a vapor-liquid process. As to the PbO$_2$ nanobelts described here, however, the growth is likely to be controlled by vapor-liquid-solid process, which has been suggested for the nanowires grown by a catalytic-assisted technique, in which a metal

15   particle is definitely located at the growth front of the wire and acts as the catalytic active site.

The dominant orientation relationship between the PbO$_2$ and the PbO is determined to be (010)$_2$ || (100)$_1$ and [101]$_2$ || [001]$_1$. Another preferable orientation of the PbO phase precipitation is 45° relative to the former case.

20   The PbO$_2$ nanobelts have been determined to be enclosed by top surfaces $\pm$(201) and side surfaces $\pm$(10$\overline{1}$). The growth direction of the nanobelts is parallel to [010], along with a typical length of several hundred micrometers, width of 50 to 300 nanometers and width-to-height ratio of 5 to 10. Each PbO$_2$ nanobelt is found to have a large polyhedral Pb

tip at its growth front, suggesting that the growth of the PbO_2 nanobelts is likely controlled by a vapor-liquid-solid mechanism. The PbO_2 nanobelts and the crystalline Pb tips are very sensitive to electron beam irradiation, resulting in the phase transformation from PbO_2 to PbO, melting of the Pb tips and formation of Pb nanocrystals under a high vacuum

5   condition.

It should be emphasized that the above-described embodiments of the present invention, particularly, any embodiments, are merely possible examples of implementations, merely set forth for a clear understanding of the principles of the invention. Many variations and modifications may be made to the above-described

10   embodiment(s) of the invention without departing substantially from the spirit and principles of the invention. All such modifications and variations are intended to be included herein within the scope of this disclosure and the present invention and protected by the following claims.